

SOP #043550B: ULTRASONIC EXTRACTION FOR BNAs/PNAs/HERBICIDES
USING METHOD 3550B

Revision: 5
Date: 03/03/06

Location: Extraction Laboratory
Semi-volatiles GC/MS Laboratory
QA Officer's Files

These procedures are restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with these techniques and methods.

1.0 SCOPE AND APPLICATION

- 1.1 This method is used for extracting nonvolatile and semivolatile base/neutral/acid (BNA), polynuclear aromatic hydrocarbon (PNA) and herbicides organic compounds from solids such as soils, sludges, and wastes. The ultrasonic process ensures intimate contact of the sample matrix with the extraction solvent.

2.0 SUMMARY OF METHOD

- 2.1 For most of samples, 2g - 30g sample (depending on the matrix; 30g is typical for a soil) is mixed with anhydrous sodium sulfate to form a free-flowing solid. Extract with methylene chloride using ultrasound. For herbicides samples, acidified sodium sulfate is used instead.
- 2.2 The extract is separated from the sample and concentrated.
- 2.3 Clean glassware and matrix cleanup procedures are used to obtain the optimum analytical chromatograms.

3.0 INTERFERENCES

- 3.1 The decomposition of some analytes has been demonstrated under basic extraction conditions. Organochlorine pesticides may de-chlorinate.
- 3.2 Degradation of PCBs, as well as more complex matrix (i.e. oil, tar, sulfur, etc.) can interfere with the "clarity" of the chromatograms.

4.0 APPARATUS AND MATERIALS

- 4.1 Apparatus for grinding dry waste samples
- 4.2 Ultrasonic device - Branson Sonifier, Model 450
- 4.3 Ultrasonic Disrupter - power wattage of 300 watts, with pulsing.
- 4.3.1 3/4" horn
- 4.3.2 Sonabox - (Ultrasonics #432B)
- 4.4 Apparatus for percent dry weight
- 4.4.1 Drying oven (105°C - 120°C)
- 4.4.2 Dessicator
- 4.4.3 Crucibles - disposable aluminum
- 4.4.4 Glass pipettes - 1ml, disposable
- 4.4.5 Beakers - 250ml
- 4.4.6 Filter paper - Whittman No. 41
- 4.5 Zymark Evaporation Station
- 4.6 Evaporation tubes
- 4.7 Water bath - Heated, capable of temperature control ($\pm 5^{\circ}\text{C}$).
- 4.8 Balance - Top-loading, capable of accurately weighing to the nearest 0.01 g.
- 4.9 Vials - 4 ml, with polytetrafluoroethylene (PTFE)-lined screw caps.
- 4.10 Glass scintillation vials - 20-mL, with PTFE-lined screw caps.
- 4.11 Tongue depressors, disposable
- 4.12 Beakers - 250ml
- 4.13 Glass funnel
- 4.14 Filter paper, coarse grade
- 4.15 Adhesive labels
- 4.16 Syringe - 5-mL NIST certified
- 4.17 250mL Erlenmeyer flasks

5.0 REAGENTS

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Note: Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

- 5.1 Sodium sulfate (granular, anhydrous), Na_2SO_4 .
- 5.2 Extraction - All solvents must be pesticide quality or equivalent
 - 5.2.1 Methylene Chloride, CH_2Cl_2 .
 - 5.2.2 Hexane, C_6H_{14} .
 - 5.2.3 Acetone, $\text{C}_3\text{H}_6\text{O}$.
- 5.3 Surrogate and matrix spiking solutions are prepared as listed in Table 1. The detailed list of compounds for each stock mixture is given in §9.
- 5.4 High purity Ether

6.0 SAMPLE CONTAINERS AND STORAGE

- 6.1 All samples for the analysis of BNAs/PNAs/Herbicides are stored in small glass containers only.
- 6.2 Approximately 2 to 30 g (depending on the matrix) of sample is needed for extraction.
- 6.3 Refrigerate at 4°C.
- 6.4 Holding Time for solid samples is 14 days to extraction and 40 days after extraction.

7.0 GLASSWARE CLEANING

Note: All glassware must be immaculate. Glassware should be cleaned as soon as possible after the extraction. A quick reference guide is posted in the extraction laboratory.

- 7.1 Immediately after use rinse glassware with the last solvent used in it. Drain it into a bottle labeled "Wash Solvent."
- 7.2 Wash well with hot water and laboratory detergent by hand.
- 7.3 Rinse three times with hot tap water followed by three times with DI water.
- 7.4 Place in dishwasher.
- 7.5 Rinse with acetone.
- 7.6 Rinse with hexane.

8.0 PROCEDURE^[1]

- 8.1 The extraction device has a minimum of 300 watts of power and is equipped with ¾" size disrupter horns.
 - 8.1.1 The horn is maintained, by inspection of the horn tip for excessive wear that would be seen as "cavities" on the bottom of the instrument.
 - 8.1.2 Samples are prepared by thorough mixing with sodium sulfate so that it forms a free-flowing solid prior to the addition of the solvent.
 - 8.1.3 Three extractions are performed with 60ml of Methylene Chloride solvent for 3 minutes each. For herbicides, use ether instead of methylene chloride.
 - 8.1.4 Extraction is performed in the specified pulse mode, and the horn tip is positioned just below the surface of the solvent yet above the sample.
 - 8.1.5 Very active mixing of the sample and the solvent must occur when the ultrasonic pulse is activated. Observe such mixing at some point during the extraction process to insure that the placement of the horn is correct.
- 8.2 Sample handling
 - 8.2.1 Sediment/soil samples - Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.
 - 8.2.2 Waste samples - Samples consisting of multiple phases are separated into two phases. Per client request one or the other phase is extracted. If both phases need to be extracted, two separate extractions are performed.

¹ Reference for this procedure is SW-846, Revision 3, December 1996 Method 3550B, Ultrasonic Extraction

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- 8.2.3 Dry waste samples amenable to grinding - Grind or drill the waste so that it either passes through a 1-mm sieve or can be extruded through a 1-mm hole. Minimum of 10g of sample should pass through the sieve.
- 8.2.4 Gummy, fibrous, or oily materials not amenable to grinding are cut, shredded, or otherwise reduced in size to allow mixing and maximum exposure of the sample surfaces for the extraction.
- 8.3 Extraction method
- 8.3.1 Weigh approximately 2-30 g of sample (depending on the matrix) into a 250-ml beaker. Record the weight to the nearest 0.1 g.
- 8.3.1.1 The default weight used is 30g for a soil sample.
- 8.3.1.2 If the sample is a solvent or an oil matrix, approximately 2g of the neat sample is put into a 4ml screw cap vial and given to the GC/MS analyst. No extraction is performed due to the exceptionally high chromatographic response of these sample types. These samples are diluted by a factor of 400:1 and analyzed directly (see Table 8, SOP: 8270B.901.doc). The relative response of this base dilution may result in a final analysis of the sample at a higher or lower net dilution.
- 8.3.2 Nonporous or wet samples (gummy or clay type) that do not have a free-flowing sandy texture must be mixed with 60 g of anhydrous sodium sulfate, using disposable tongue depressors. If required, more sodium sulfate may be added. After addition of sodium sulfate, the sample should be free flowing.
- 8.3.3 a) For BNA extraction: Add 1.0 ml of the BNA surrogate standard solution to all samples, spiked samples, QC samples, and blanks (see Table 1).
b) For PNA extraction: Add 1.0 ml of the PNA surrogate standard solution to all samples. Spiked samples, QC samples, and blanks (see Table 1).
c) For DRO extraction: Add 1.0 ml of the DRO surrogate standard solution to all samples. Spiked samples, QC samples, and blanks (see Table 1).
d) For herbicides extraction: Add 1.0 ml of the HERB surrogate standard solution to all samples. Spiked samples, QC samples, and blanks (see Table 1).
- 8.3.4 For the sample in each batch selected for spiking (*i.e.* LCS, MS, MSD), add 1.0 ml of the matrix spiking solution (BNA, PNA, DRO, or HERB as appropriate, see Table 1).
- 8.3.5 Place the bottom surface of the tip of the 3/4 inch disrupter horn about 1/2 inch below the surface of the solvent, but above the sediment layer.
- 8.3.6 Extract ultrasonically for 3 minutes, with output control knob set at 6 and with mode switch on Pulse (pulsing energy rather than continuous energy) and percent-duty cycle knob set at 50% (energy on 50% of time and off 50% of time).
- 8.3.7 Decant through a conical gravity filter (Whatman No. 41 filter paper) and sodium sulfate to catch any excess water into an evaporation tube. For herbicides, decant into a 250mL Erlenmeyer flask with 10-15g acidified sodium sulfate.
- 8.3.8 Repeat the extraction with two additional 60 ml portions of methylene chloride. Pour off the solvent after the ultrasonic extraction. On the final ultrasonic extraction, pour the entire sample onto the filter with extraction solvent.
- 8.3.9 For herbicides, let the 250 mL Erlenmeyer flask stand with occasional swirling for two hours. Transfer the extract to an evaporation tube.
- 8.4 Evaporation method
- 8.4.1 Place the concentrator tube in the TurboVap Evaporation Station, that has the water bath at 42±2°C, 21 psi, until the extract reaches a 1 ml final volume.
- 8.4.2 Transfer the sample extract to a 4 ml pre-calibrated vial. Adjust to 1 ml final volume.
- 8.4.3 For herbicides follow the diazomethane methylation procedure outlined in the diazomethane generation SOP.

9.0 QUALITY CONTROL

- 9.1 Samples are extracted in batches of 20 samples or less. For every batch there should be a Blank, LCS, MS, and MSD/DUP depending on the clients request. All the reagent blanks, matrix spikes, or replicate samples should be subjected to exactly the same analytical procedures as those used on actual samples. In

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case of the client not providing the necessary sample volume to perform the required QC samples, equivalent laboratory matrix samples can be analyzed.

- 9.2 The B/N surrogate standard must contain the following compounds: Nitrobenzene-d5, 5,000 ug/ml (CAS 4165-60-0), 2-fluorobiphenyl, 5,000 ug/ml (CAS 321-60-8), p-terphenyl-d14, 5,000 ug/ml (CAS 1718-51-0). Cat. No. 31086, RESTEK (800-356-1688). The Acid surrogate standard must contain the following compounds: 2-fluorophenol, 10,000 ug/ml (CAS 367-12-4), Phenol-d6, 10,000 ug/ml (CAS 13127-88-3), 2,4,6-tribromophenol, 10,000 ug/ml (CAS 118-79-6). Cat. No. 31087, RESTEK (800-356-1688). The concentrations listed are those in the stock spiking solutions. [the Acid surrogate standard is N/A for the PNA method.] The surrogate standard is prepared according to Table 1.
- 9.3 The B/N MS/MSD and LCS spikes will contain the following compounds; Acenaphthene, 5,000 ug/ml (CAS 83-32-9), 1,4-dichlorobenzene, 5,000 ug/ml (CAS 106-46-7), 2,4-dinitrotoluene, 5,000 ug/ml (CAS 121-14-2), n-nitroso-di-n-propylamine, 5,000 ug/ml (CAS 621-64-7), Pyrene, 5,000 ug/ml (CAS 129-00-0), 1,2,4-trichlorobenzene, 5,000 ug/ml (CAS 120-82-1). Cat. No. 31074, RESTEK (800-356-1688). The Acid MS/MSD and LCS spikes will contain the following compounds: 4-chloro-3-methylphenol, 10,000 ug/ml (CAS 59-50-7), 2-chlorophenol, 10,000 ug/ml (CAS 95-57-8), 4-nitrophenol, 10,000 ug/ml (CAS 100-02-7), pentachlorophenol, 10,000 ug/ml (CAS 87-86-5), phenol, 10,000 ug/ml (CAS 108-95-2). Cat. No. 31061/31071, RESTEK (800-356-1688). The concentrations listed are those in the stock spiking solutions. MS/MSD spike should be prepared at a concentration at or below the medium level of the BNA curve. The MS/MSD and LCS standards are prepared according to Table 1.
- 9.4 The PNA MS/MSD and LCS spikes will contain the following compounds; Naphthalene, 2,000 ug/ml, 2-Methylnaphthalene, 2,250 ug/ml, Acenaphthylene, 2,000 ug/ml, Acenaphthene, 2,000 ug/ml, Flourene, 2,000 ug/ml, Phenanthrene, 2,000 ug/ml, Anthracene, 2,000 ug/ml, Flouranthene, 2,000 ug/ml, Pyrene, 2,000 ug/ml, Benzo (a) anthracene, 2,000 ug/ml, Chrysene, 2,000 ug/ml, Benzo (b) flouranthene, 2,000 ug/ml, Benzo (k) flouranthene, 2,000 ug/ml, Benzo (a) pyrene, 2,000 ug/ml, Indeno (1,2,3-cd) pyrene, 2,000 ug/ml, Dibenzo (ah) anthracene, 2,000 ug/ml, Benzo(ghi) perylene, 2,000 ug/ml. The concentrations listed are those in the stock spiking solutions. MS/MSD spike should be prepared at a concentration at or below the medium level of the PNA curve. The MS/MSD and LCS standards are prepared according to Table 1.
- 9.5 The DRO MS/MSD and LCS spikes contains neat diesel fuel diluted to a concentration appropriate for the sensitivity of the GC/MS (1000 mg/L). The MS/MSD and LCS standards are prepared according to Table 1.
- 9.6 New lot blanks are analyzed to insure the purity of the materials and reagents.

Note: The working standards are prepared every six to 12 months or when evidence of bias or trends are observed to show that the standards need to be replaced.

10.0 DOCUMENTATION

- 10.1 All pertinent information is entered into an extraction logbook (See Table 1). The extraction log sheet has to contain the following information on the header/table:

- Date
- ANALYSTS INITIALS
- Method
- Surrogate/MS/MSD/LCS standard unique traceability ID
- Methylene Chloride #
- Sample #
- Matrix
- Sample weight
- Solvent ID & Volume (ml)
- Final extract volume

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- Surrogate standard spike volume
- MS spike volume

11.0 REFERENCES

11.1 Method 3550A SW

12.0 APPROVAL & ISSUE

12.1 The following personnel have read, accepted and approved this standard operating practice:

Analyst

Date

Andy Ball, QA Officer

Date

Maya V. Murshak, Technical Director

Date

13.0 Tables

Table 1. Surrogate and Spike Preparation for use in Extraction

BNA Surrogate:

For 100 ml total solution at 100 mg/L:
97 ml of Acetone
1 ml of 10,000 mg/L Acids surrogate
2 ml of 5,000 mg/L B/N surrogate

BNA MS Spike:

For 20 ml total solution at 50 mg/L:
19.7 ml of Acetone
100 ul of 10,000 mg/L Acids spike
200 ul of 5,000 mg/L B/N spike

PNA/DRO Surrogate:

For 100 ml total solution at 100 mg/L:
98 ml of Acetone
2 ml of 5,000 mg/L B/N surrogate

PNA MS Spike:

For 20 ml total solution at 50 mg/L:
19.1 ml of Acetone
500 ul of 2,000 mg/L PNA stock
444 ul of 2250 mg/L 2-Methylnaphthalene stock

DRO MS Spike:

For 20 ml total solution at 1000 mg/L;
20.0 ml of Acetone
20.0 mg of neat Diesel Fuel (gravimetric preparation)